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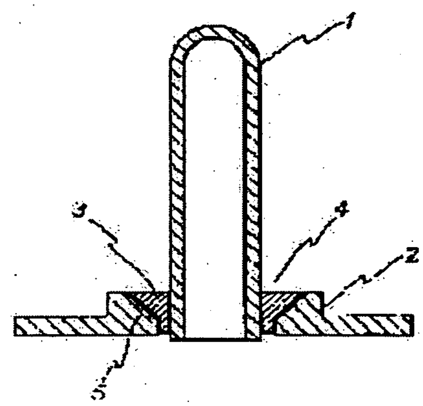
(54) METHOD FOR SEALING CELL PART OF OXYGEN SENSOR

(57)Abstract:
PURPOSE: To provide an oxygen sensor which can improve airtightness and durability, can measure oxygen concentration accurately even under low or high concentration accurately, and further is rich in durability without fault and its manufacturing method.
CONSTITUTION: When sealing a stabilization zirconia 1 at the cell part of an oxygen sensor and a mounting fitment 2 made of corrosion resistance alloy, a covering film 5 consisting of nickel alloy containing active metal is formed on the surface where at least a sealing part 4 is formed of the mounting fitment 2 made of corrosion resistance alloy, a sealing material 3 consisting of alumino silicate glass is filled into the sealing part 4 formed between the stabilization zirconia and the mounting fitment 2 made of the corrosion resistance metal where the covering film 5 is formed, and then the cell part is sealed at a temperature exceeding the flexibility point of the sealing material 3.



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CLAIMS

[Claim(s)]
[Claim 1] It faces sealing between the fully-stabilized-zirconia member of the cel part of an oxygen sensor, and the fixing metal made from an anticorrosion alloy. The aforementioned fully-stabilized-zirconia member after forming the covering film which consists of a nickel alloy containing an active metal in the front face of the fixing metal made from said anticorrosion alloy which forms the sealing section at least, The sealing approach of the cel part of the oxygen sensor characterized by sealing by being filled up with the sealing material which becomes the sealing section formed between the fixing metal made from an anticorrosion alloy with which said covering film was formed from aluminosilicate glass, and heating to the temperature more than the softening temperature of this sealing material.
[Claim 2] The covering film which consists of a nickel alloy containing said active metal is the sealing approach of the cel part of the oxygen sensor according to claim 1 characterized by being the sum total and containing at least one sort in an active metal 0.5 to 30% of the weight.
[Claim 3] The covering film which consists of a nickel alloy containing said active metal is the sealing approach of the cel part of the oxygen sensor according to claim 1 characterized by being the sum total, containing at least one sort in an active metal 0.5 to 30% of the weight, and containing Lynn (P) 20 or less % of the weight.
[Claim 4] a means to form said covering film be the sealing approach of the cel part of the oxygen sensor according to claim 1 characterize by be because the nickel alloy powder or the mixed powder which contain an active metal and nickel at least containing an active metal be apply to the front face of the fixing metal made from an anticorrosion alloy which form the sealing section at least and it heat-treat among a non-oxidizing atmosphere at the temperature more than the melting point of the aforementioned alloy powder or said mixed powder .
[Claim 5] Said aluminosilicate glass is the sealing approach of the cel part of the oxygen sensor according to claim 1 which contains 40 - 75 % of the weight of silicas, contains an alumina three to 35% of the weight, is the sum total and contains at least one sort in MgO, MnO, CaO, SrO, PbO, BaO, ZnO, Li2O, Na2O, K2O, and Rb2O five to 30% of the weight further.
[Claim 6] Said aluminosilicate glass contains 40 - 75 % of the weight of silicas, and contains an alumina three to 35% of the weight. At least one sort in MgO, MnO, CaO, SrO, PbO, BaO, ZnO, Li2O, Na2O, K2O, and Rb2O furthermore, in total The sealing approach of the cel part of the oxygen sensor according to claim 1 characterized by containing five to 30% of the weight, and containing at least one of B-2 O3 and P2O5 sorts 15 or less % of the weight in total further.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the sealing approach for sealing the fully stabilized zirconia of the cel part of an oxygen sensor, and the fixing metal made from an anticorrosion alloy in a detail further about the sealing approach of the cel part of an oxygen sensor.
[0002]
[Description of the Prior Art] The oxygen sensor using the fully stabilized zirconia in which the yttria as current and a stabilizing agent etc. carried out specified quantity dissolution is used with a boiler, a pro cel heater, an inert gas generator, cement baking kiln, lime calcination kiln, a glass fusion furnace, a heating furnace, a soaking pit, a heat treating furnace, a reducing atmosphere furnace, a shaft furnace, etc., and is used under the environment with cruel corrosive gas, elevated temperature, high humidity, etc. And sealing of the flanges made from a nickel alloy, such as the cel part of fully stabilized zirconia and the fixing metal made from an anticorrosion alloy with which the oxygen sensor for these contains Y_2O_3 to eight-mol %, for example, Hastelloy etc., is carried out with the inorganic system binder.
[0003] Since the oxygen sensor using this fully stabilized zirconia is constituted using the difference of the electromotive force produced according to the oxygen density difference of the reference gas and measurement gas which exist within and without a cel septum so that an oxygen density may be measured, the airtight quality of the sealing section of a cel member and fixing metal influences the accuracy of measurement of an oxygen density greatly.
[0004] however, in the conventional oxygen sensor sealed using ** et al. and an inorganic system binder It is easy to generate airtight [poor] in the sealing section, and since the yield is bad, it is easy to become the cause of a cost rise. Moreover, since the airtightness of a good process also has the amount of leaks very as bad as a 1x10-2 atm-cc/second The accuracy of measurement of an oxygen density and the accuracy of measurement of the oxygen density under the high concentration near 21% of concentration under the low concentration of ppm order and in atmospheric air and near 100% especially are bad, and it becomes difficult to measure an oxygen density with a sufficient precision.
[0005] Furthermore, since airtightness was bad, when it was used under the ambient atmosphere of corrosive gas, corrosive gas trespassed upon the interior of a sensor, and the internal device corroded, it became the cause of failure, and there was un-arranging [that the endurance of an oxygen sensor fell].
[0006]
[Problem(s) to be Solved by the Invention] Therefore, this invention was accomplished in view of the above technical situations, airtightness and its endurance improve, and also under low concentration and high concentration, it can measure an oxygen density with a sufficient precision, and aims at offering the oxygen sensor which is rich in endurance with still less failure, and its process.
[0007]
[Means for Solving the Problem] This invention is faced sealing between the fully-stabilized-zirconia member of the cel part of an oxygen sensor, and the fixing metal made from an anticorrosion alloy. The aforementioned fully-stabilized-zirconia member after forming the covering film which consists of a nickel alloy containing an active metal in the front face of the fixing metal made from said anticorrosion alloy which forms the sealing section at least, The sealing approach of the cel part of the oxygen sensor characterized by sealing is offered by being filled up with the sealing material which becomes the sealing section formed between the fixing metal made from an anticorrosion alloy with which said covering film was formed from aluminosilicate glass, and heating to the temperature more than the softening temperature of this sealing material.
[0008] Formation of the covering film which consists of a nickel alloy which contains an active metal here is for improving the wettability to the anticorrosion alloy of aluminosilicate glass, and may seal both good with

aluminosilicate glass by improving wettability. For example, by forming the above-mentioned covering film in advance of sealing, the contact angle of melting aluminosilicate glass and Hastelloy can be made to decrease at 70 degrees from 110 degrees (wettability improvement), and sealing of the airtightness of the sealing section and endurance which improved sharply becomes possible. In addition, in this invention, the compound which contains a very activity metal and this metal to the oxygen of Ti, Zr, Hf, Cr, Be, TiH2, and ZrH2 grade is called an active metal.

[0009] Moreover, although well-known means, such as a CVD method, the sputtering method, and a spraying process, are employable as means forming of the above-mentioned covering film, it is suitable to adopt a means according to claim 3 from a viewpoint of partial covering to an inside like a sealing part, as shown in the following. Moreover, as for the heat treatment time amount for sealing with said aluminosilicate glass, it is desirable that it is 15 minutes or more, and it is suitable for it to make a heat treatment ambient atmosphere into an inert gas ambient atmosphere, for example, nitrogen-gas-atmosphere mind. Since an anticorrosion alloy will oxidize at the time of sealing, sealing material foams in a vacuum ambient atmosphere or a reducing atmosphere and the sealing section serves as porosity in an oxidizing atmosphere, it is not suitable.

[0010] Furthermore, the viscosity of aluminosilicate glass becomes moderate and it is more suitable for the heat treatment temperature for sealing with aluminosilicate glass than the softening temperature of the aluminosilicate glass as sealing material from the point of sealing nature to consider as temperature high about 100-150 degrees C. Furthermore, it is suitable for the softening temperature of said aluminosilicate glass that it is 400 degrees C or more. The reason is that a part for the cel point of an oxygen sensor is heated by 750 degrees C of abbreviation for oxygen density measurement, and the temperature of the sealing section rises to about 350 degrees C of abbreviation in connection with it. There is a possibility that a cel part may separate from fixing metal that the softening temperature of the aluminosilicate glass used as sealing material is less than 400 degrees C. From the above thing, airtightness and endurance improve, also under low concentration and high concentration, an oxygen density can be measured with a sufficient precision and manufacture of the oxygen sensor which is rich in endurance with still less failure is attained.

[0011] And it is suitable for the covering film which consists of a nickel alloy containing an active metal to be the sum total and to contain at least one sort in an active metal 0.5 to 30% of the weight. Since the content of an active metal becomes the inclination for the effectiveness of improving wettability with aluminosilicate glass to fall at less than 0.5 % of the weight here, the covering film which will be obtained if the content of an active metal, on the other hand, exceeds 30 % of the weight becomes weak, and coefficient of thermal expansion becomes low as compared with the anticorrosion alloy as a base material, and a crack arises or it exfoliates, it is not suitable.

[0012] Furthermore, it is suitable for the covering film which consists of a nickel alloy containing an active metal to be the sum total, to contain at least one sort in an active metal 0.5 to 30% of the weight, and to contain Lynn (P) 20 or less % of the weight. namely, the nickel alloy containing an active metal -- further -- Lynn -- in order for adding (P) 20 or less % of the weight to lower the melting point of the nickel alloy containing an active metal, to raise the fluidity at the time of melting further and to make formation of the covering film easy -- it is -- Lynn -- if the content of (P) exceeds 20 % of the weight, since the covering film obtained will become weak and will exfoliate, it is not suitable.

[0013] A means to form the covering film is because the nickel alloy powder or the mixed powder which contains an active metal and nickel at least containing an active metal is applied by the proper approach and heat-treated under a non-oxidizing atmosphere at the temperature more than the aforementioned alloy powder or the melting point of the mixed powder on the front face of the fixing metal made from an anticorrosion alloy which forms the sealing section at least. The temperature for this heat treatment is 800-1000 degrees C. Although the non-oxidizing atmosphere to be used can mention a reducing atmosphere or a vacuum ambient atmosphere, the ambient atmosphere of a vacuum 10 to 4 torrs or less is suitable for it especially. The flow of the fused active metal content nickel alloy becomes good, and the airtightness of formation of the covering film under a vacuum ambient atmosphere of the sealing section improves.

[0014] Furthermore, about the presentation of aluminosilicate glass, what contains 40 - 75 % of the weight of silicas, contains 3 - 35 % of the weight of aluminas, is the sum total and contains at least one sort in MgO, MnO, CaO, SrO, PbO, BaO, ZnO, Li2O, Na2O, K2O, and Rb2O five to 30% of the weight further is suitable. Here, when it is hard to vitrify the silica content of aluminosilicate glass completely, and it crystallized in part at less than 40 % of the weight, a presentation tends to become heterogeneity and the load of the heat cycle is carried out, it is easy to generate a crack by distortion inside glass, and there is an inclination for endurance to fall. On the other hand, if a silica content exceeds 75 % of the weight, a coefficient of thermal expansion will fall, and it will be easy to generate a crack at the time of cooling after sealing under an elevated temperature, and measurement of an oxygen density, and will become the inclination for yield to fall, as a product.

[0015] Moreover, at less than 3 % of the weight, the chemical durability over corrosive gas etc. deteriorates, and-on the other hand, the alumina content of aluminosilicate glass is in the inclination for a coefficient of thermal expansion to fall, and to become easy to generate a crack and for the yield as a product to fall at the time of cooling after sealing under an elevated temperature, and oxygen density measurement, when an alumina content exceeds 35 % of the weight.

[0016] Furthermore, the viscosity of aluminosilicate glass becomes suitable and it is suitable for heat treatment temperature required for sealing with aluminosilicate glass to consider as temperature higher about 100-150 degrees C than the softening temperature of the aluminosilicate glass as sealing material. Moreover, 400 degrees C or more are suitable for aluminosilicate glass softening temperature. The reason is that a part for the point of the cel part of an oxygen sensor is heated by about 700 degrees C for oxygen density measurement, and the temperature of the sealing section rises to about about 350 degrees C in connection with it. There is risk of a cel part separating from fixing metal that the softening temperature of the aluminosilicate glass used as sealing material is less than 400 degrees C.

[0017] moreover, in order to double the coefficient of thermal expansion of aluminosilicate glass with coefficient-of-thermal-expansion (10x10-6/degree C) extent of fully stabilized zirconia On aluminosilicate glass, at least one sort in MgO, MnO, CaO, SrO, PbO, BaO, ZnO, Li2O, Na2O, K2O, and Rb2O in total Even if it is desirable to add five to 30% of the weight and it is over 30 % of the weight at least less than 5% of the weight, it is hard coming to have consistency a coefficient of thermal expansion with it of fully stabilized zirconia, and is in the inclination a crack becomes easy to generate at the time of cooling after sealing under an elevated temperature, and oxygen density measurement.

[0018] About the presentation of aluminosilicate glass, 40 - 75 % of the weight of silicas is contained. It contains 3 - 35 % of the weight of aluminas. Further at least one sort in MgO, MnO, CaO, SrO, PbO, BaO, ZnO, Li2O, Na2O, K2O, and Rb2O in total What is the sum total and contains at least one of B-2 O3 and P2O5 sorts 15 or less % of the weight further in what was contained five to 30% of the weight is suitable. Since this makes the chemical durability over corrosive gas etc. increase, it adds, if an addition exceeds 15 % of the weight, a coefficient of thermal expansion will fall, and it is easy to generate a crack at the time of cooling after sealing under an elevated temperature, and oxygen density measurement, and it is in the inclination for the yield as a product to fall.

[0019] In addition, as the quality of the material of the anticorrosion alloy which forms fixing metal, the alloy containing nickel, such as Hastelloy, is desirable.

[0020]

[Function] Formation of the covering film which consists of a nickel alloy containing an active metal improves the wettability to the anticorrosion alloy of aluminosilicate glass, can seal the fully stabilized zirconia of the cel member of an oxygen sensor, and the fixing metal made from an anticorrosion alloy good with aluminosilicate glass, contributes them to improvement in the airtightness of the sealing section, and endurance further, and yield's of a product improves.

[0021] Moreover, by specifying the presentation of the covering film which consists of a nickel alloy containing an active metal as the above range, the wettability to the anticorrosion alloy of aluminosilicate glass is improved further, and it may seal in an airtight more more firmly.

[0022] Furthermore, further, by [of the above / Lynn] carrying out range content, to the presentation of the covering film which consists of a nickel alloy containing an active metal, the melting point of the nickel alloy containing an active metal is lowered, the fluidity at the time of melting is raised, formation of the covering film is made easy, the wettability to the anticorrosion alloy of aluminosilicate glass is improved sharply, and it may seal more more firmly in it at an airtight.

[0023] Furthermore, it becomes easy [partial covering to an inside like a sealing part] by using the covering film which consists of a nickel alloy containing an active metal.

[0024] Furthermore, since the sealing part which a part for the cel point of an oxygen sensor is heated by about 750 degrees C for oxygen density measurement, therefore seals the fully stabilized zirconia of the cel member of an oxygen sensor and the fixing metal made from an anticorrosion alloy is also exposed to a remarkable elevated temperature, as sealing material, it is necessary to excel in thermal resistance and thermal shock resistance. Moreover, since a coefficient of thermal expansion is 10x10-6/degree C, that [fully stabilized zirconia's] in which sealing material also has a comparable coefficient of thermal expansion is desirable. Furthermore, the environment which uses an oxygen sensor is a corrosive gas ambient atmosphere in many cases, and sealing material needs to excel also in corrosion resistance. Making it such, the aluminosilicate glass as sealing material has fully satisfied these terms and conditions.

[0025] Furthermore, the presentation of the aluminosilicate glass as sealing material makes the chemical durability over corrosive gas etc. increase by specifying it as the aforementioned range.

[0026] As mentioned above, according to the sealing approach of this invention, airtightness and endurance of an oxygen sensor improve, also under low concentration and high concentration, an oxygen density can be measured with a sufficient precision and the oxygen sensor which is rich in endurance with still less failure can be offered.
[0027] Next, this invention is not limited by them although an example explains concretely the sealing approach of the cel part of the oxygen sensor of this invention.
[0028]
[Example] It prepared so that purity might serve as a presentation (No.1-43) which shows red phosphorus to the 1st column (presentation of the covering film) of Tables 1 and 2 if needed [the nickel powder, the active metal powder, and if needed] which are 99.9%, and with the agate mortar, it mixed with the screen oil and considered as the slurry. 120 degrees C of covering film which consists of a nickel alloy containing an active metal were formed by the vacuum dryer by heat-treating for 20 minutes in a 800-1000-degree C temperature requirement in a vacuum ambient atmosphere [10 below -4 torrs (torr)], after drying for 30 minutes by applying this slurry to the sealing part of the fixing metal made from a nickel alloy (Hastelloy).
[0029] On the other hand, the aluminosilicate glass used as sealing material was manufactured as follows. That is, it prepared so that it might become the presentation (No.1-43) which shows each reagent powder of 99.9% of purity to the 2nd column (presentation of sealing material) of Tables 1 and 2, and using the planetary mill, it ground for 6 hours and mixed. After dropping underwater, having made it quench, after putting this mixed powder into the platinum crucible and carrying out melting all over an oxidation furnace, and grinding, grain size was arranged by the screen of 300 meshes, and it considered as the sealing material by this invention.
[0030] With the agate mortar, it mixed with polyvinyl butyral resin and the above sealing material was made into the slurry. After filling up with a slurry the sealing part formed between the fully stabilized zirconia which is the cel member of an oxygen sensor, and the fixing metal made from a nickel alloy (Hastelloy) with which the covering film was formed, 120 degrees C dried by the vacuum dryer for 1 hour. Then, at the oxidation furnace, it held at 350 degrees C for 2 hours, and cleaning in glass was performed. And the sealing activity was done in nitrogen-gas-atmosphere mind by heat-treating at temperature high 100 degrees C respectively from the glass softening temperature of each sealing material (No.1-43). in addition, fully stabilized zirconia -- Y_2O_3 as a stabilizing agent -- 18-mol % -- it contains.
[0031] As mentioned above, using respectively the covering film prepared by the presentation shown in Tables 1 and 2, and sealing material (No.1-43), oxygen sensor components (cel member) were manufactured, and by viewing, the existence of the crack of a sealing member was observed and was summarized to the 1st of the 3rd column (evaluation result) of Tables 1 and 2. And to the oxygen sensor components with which existence of a crack is not accepted in the sealing section, the helium leak detector (the product made from Japanese ** Anelva; ASM-151T, limit-of-detection;2x10-10 torr) estimated airtightness, and it was shown in the 2nd of the column of an evaluation result.
[0032] Airtightness a furnace atmosphere as durability test to good oxygen sensor components moreover, in 10% of SO_2, and the nitrogen gas containing 5% of O_2 After repeating the heat cycle which cools to a room temperature by part for cooling rate/of 35 degrees C, and is held for 1 hour after carrying out a temperature up and holding to 350 degrees C by part for programming-rate/of 35 degrees C for 2 hours 100 times, the above pneumatic tests were performed and the evaluation trial of checking the existence of leak was performed. The result of this evaluation trial is shown in the 3rd endurance of the column of an evaluation result.
[0033] Each evaluation result is shown in the 3rd column (evaluation result) of Tables 1 and 2. Moreover, the evaluation result when sealing as an example of a comparison (No.44) with the conventional inorganic system binder (SUMISERAMU S-301; trade name) is also collectively shown in Tables 1 and 2. In addition, the figure of the column of an evaluation result used the number of excellent articles as the molecule, and showed the evaluation number to the denominator.
[0034]
[Table 1]

評価試験

No.	被覆膜の組成 (wt%)			封着材の組成 (wt%)						評価結果		
	Ni	活性金属	P	SiO_2	Al_2O_3	第3成分			B_2O_3 or P_2O_5 *	クラック (なし)	気密性 (リークなし)	耐久性 (リークなし)
						BaO	CaO	その他				
1	89.9	Cr; 0.1	10.0	62.1	20.0	17.3	–	–	–	10/10	7/10	4/5
2	89.5	Cr; 0.5	10.0	61.5	22.4	15.1	–	–	–	10/10	10/10	10/10
3	89.0	Cr; 1.0	10.0	63.3	20.3	16.0	–	–	–	10/10	10/10	10/10
4	85.0	Cr; 5.0	10.0	65.2	18.7	15.5	–	–	–	10/10	10/10	10/10
5	80.0	Cr; 10.0	10.0	63.7	19.3	–	16.1	–	–	10/10	10/10	10/10
6	75.0	Cr; 15.0	10.0	62.2	22.7	–	–	MgO; 14.5	–	10/10	10/10	10/10
7	60.0	Cr; 30.0	10.0	62.8	20.3	16.0	–	–	–	10/10	10/10	10/10
8	55.0	Cr; 35.0	10.0	60.9	21.3	17.1	–	–	–	8/10	9/10	7/9
9	85.0	Cr; 15.0	–	62.2	22.7	–	–	MgO; 14.5	–	8/10	9/10	9/10
10	75.0	Ti; 10.0	15.0	60.2	21.3	18.4	–	–	–	10/10	10/10	10/10
11	75.0	Zr; 10.0	15.0	59.7	20.4	19.3	–	–	–	10/10	10/10	10/10
12	75.0	Be; 10.0	15.0	63.2	18.6	17.9	–	–	–	10/10	10/10	10/10
13	95.0	Cr; 5.0	–	63.8	19.2	16.5	–	–	–	8/10	8/10	8/10
14	94.0	Cr; 5.0	1.0	63.1	20.6	16.0	–	–	–	10/10	10/10	10/10
15	85.0	Cr; 10.0	5.0	63.2	22.3	14.0	–	–	–	10/10	10/10	10/10
16	65.0	Cr; 15.0	20.0	63.8	20.3	16.1	–	–	–	10/10	10/10	10/10
17	45.0	Cr; 30.0	25.0	63.2	20.3	15.8	–	–	–	10/10	6/10	3/6
18	75.0	Cr; 15.0	10.0	34.2	32.5	28.3	–	–	B; 3.7	10/10	10/10	7/10
19	75.0	Cr; 15.0	10.0	46.5	20.4	27.3	2.5	–	P; 3.1	10/10	10/10	10/10
20	75.0	Cr; 15.0	10.0	48.2	19.7	14.1	7.2	SrO; 6.9	B; 2.6	10/10	10/10	10/10
21	75.0	Cr; 15.0	10.0	54.8	21.3	14.5	3.2	SrO; 3.0	P; 2.8	10/10	10/10	10/10
22	75.0	Cr; 15.0	10.0	63.2	20.3	–	–	MgO; 14.0	B; 3.4	10/10	10/10	10/10
23	75.0	Cr; 15.0	10.0	74.5	11.3	9.3	–	–	P; 3.7	10/10	10/10	10/10
24	75.0	Cr; 15.0	10.0	80.1	12.6	3.2	–	–	B; 3.2	7/10	6/6	6/6
25	85.0	Cr; 15.0	–	54.8	21.3	14.5	3.2	SrO; 3.0	P; 2.8	9/10	9/10	8/10

* B; B_2O_3　P; P_2O_5を示す。

[0035]
[Table 2]

評価試験

No.	被覆膜の組成 (wt%) Ni	活性金属	P	封着材の組成 (wt%) SiO₂	Al₂O₃	第3成分 BaO	CaO	その他	B₂O₃ or P₂O₅ *	評価結果 クラック(なし)	気密性(リークなし)	耐久性(リークなし)
26	75.0	Cr;15.0	10.0	57.0	1.1	14.8	10.0	SrO;13.1	B; 3.7	10/10	10/10	7/10
27	75.0	Cr;15.0	10.0	56.1	3.2	15.2	10.3	SrO; 4.1	B;10.5	10/10	10/10	10/10
28	75.0	Cr;15.0	10.0	53.5	10.5	−	19.5	SrO; 8.0	B; 8.3	10/10	10/10	10/10
29	75.0	Cr;15.0	10.0	52.1	18.1	15.2	4.0	SrO; 5.0	B; 5.2	10/10	10/10	10/10
30	75.0	Cr;15.0	10.0	53.3	22.5	15.5	3.2	SrO; 2.3	B; 1.7	10/10	10/10	10/10
31	75.0	Cr;15.0	10.0	54.1	34.2	10.1	−	−	−	10/10	10/10	10/10
32	75.0	Cr;15.0	10.0	52.9	38.2	6.5	−	−	B; 1.8	7/10	7/7	7/7
33	75.0	Cr;15.0	10.0	52.3	5.1	28.7	−	−	B;13.2	10/10	10/10	10/10
34	85.0	Cr;15.0	−	52.6	5.3	26.1	−	−	B;14.3	9/10	8/10	9/10
35	75.0	Cr;15.0	10.0	53.1	5.0	23.6	−	−	B;17.5	8/10	8/8	7/8
36	75.0	Cr;15.0	10.0	50.5	21.2	15.0	−	MgO; 9.2	B; 3.1	10/10	10/10	10/10
37	75.0	Cr;15.0	10.0	50.3	20.3	14.3	−	ZnO;11.8	P; 2.1	10/10	10/10	10/10
38	75.0	Cr;15.0	10.0	49.5	22.2	16.1	−	MnO; 9.0	B; 2.5	10/10	10/10	10/10
39	75.0	Cr;15.0	10.0	48.0	23.1	16.0	−	PbO; 9.2	P; 2.7	10/10	10/10	10/10
40	75.0	Cr;15.0	10.0	60.5	15.2	14.0	−	LiO₂; 9.2	−	10/10	10/10	10/10
41	75.0	Cr;15.0	10.0	62.3	16.3	10.3	−	Na₂O;11.8	−	10/10	10/10	10/10
42	75.0	Cr;15.0	10.0	59.5	15.2	16.1	−	K₂O ; 9.0	−	10/10	10/10	10/10
43	75.0	Cr;15.0	10.0	63.0	17.1	10.0	−	Rb₂O; 9.2	−	10/10	10/10	10/10
44	従来品；無機接着材による封着									6/10	3/6**	1/3**

* B；B_2O_3 P；P_2O_5を示す。
** 従来品の気密試験は、リーク量、2×10^{-2} atm・cc／sec以下として測定した。

[0036] From the above result, airtightness has been improved more than ten (8th power of minus) as compared with elegance (No.42 and amount of leaks;1x10-2 atm-cc/second) conventionally which it was checked that all airtightness is good by the limit-of-detection 2x10-10 atm-cc/second, and sealed the oxygen sensor components (No.1-43) of this invention with the conventional technique.
[0037] Moreover, it was checked using the helium leak detector that each oxygen sensor component (No.1-43) with which airtightness was checked in the range of limit of detection is measurable with a sufficient precision in the low concentration field to oxygen density 1ppb, 21% of oxygen densities, and the oxygen density in the high-density area near 100% of oxygen densities.
[0038] In addition, in elegance (No.44), it was checked conventionally which was sealed with the inorganic system binder that the airtightness of the sealing section is poor, the accuracy of measurement 0.1% or less of oxygen densities, near 21% of oxygen densities, and near 100% of oxygen densities is bad, and measurement of

an exact oxygen density is difficult.

[0039]

[Effect of the Invention] As explained above, the following remarkable technical effectiveness was acquired by the sealing approach of the oxygen sensor of this invention. The wettability to the anticorrosion alloy of aluminosilicate glass has been improved by formation of the nickel alloy covering film which contains [1st] an active metal, the airtightness of the sealing section improved sharply, the oxygen sensor which can measure an oxygen density with a sufficient precision also under low concentration and high concentration was obtained, further, the yield was high and the oxygen sensor with which failure is rich in endurance few was obtained. Further, according to the adhesion approach of the oxygen sensor of this invention, a production cost falls in the 2nd and the commercial scene of an oxygen sensor is expanded to it.

[Translation done.]

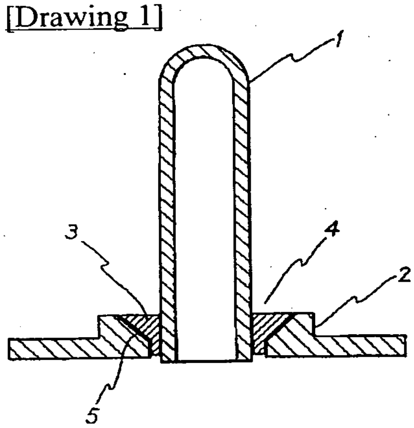
DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is the sectional view showing the cross section of the cel part of the oxygen sensor by this invention.
[Description of Notations]
1 Cel made from Fully Stabilized Zirconia
2 Fixing Metal made from Anticorrosion Alloy
3 Adhesion Material
4 Holdfast
5 Covering Film

[Translation done.]

DRAWINGS

[Drawing 1]



[Translation done.]